Energy levels of semiconductor surface vacancies

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We present calculations of the bound state energy levels of anion vacancies near the surface of a III–V semiconductor. We consider the (110) surface of GaAs, InP, and the $Ga_{1-x}Al_xAs$ alloy system. As the vacancy is moved toward the surface, the energy levels are only slightly perturbed until the vacancy reaches the second atomic layer from the surface. At this point, the anion vacancy levels move to lower energy. We find that there is a general trend in the vacancy energy levels with semiconductor ionicity. As the material becomes more ionic, the anion vacancy levels move to higher energy. Comparing this trend with experimentally observed Schottky barrier heights, we find a strong correlation between the position of the highest occupied level in the anion vacancy and the measured Fermi level at the surface. This result suggests that the recently proposed defect model is capable of accounting for observed trends in Schottky barrier formation.

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I. INTRODUCTION

It has recently been proposed that defects near the semiconductor surface determine the Schottky barrier height in III–V semiconductors.[1–4] In this model, these defects induce localized electronic states whose energies lie in the semiconductor band gap. These states then pin the Fermi level at the energy of the defect level. Motivated by this proposal, we investigate the energy levels of a simple vacancy near the surface of a III–V semiconductor. Because anion material is found to be preferentially lost at the surface in several III–V semiconductors, we concentrate on anion vacancies.[1–3,5,6] We compute the vacancy energy level as a function of distance from the (110) surface. We consider the position of the vacancy levels in III–V semiconductors of varying ionicity.

The paper is organized in the following way: in Sec. II, we discuss qualitatively the bound state energy levels of an anion vacancy in a III–V semiconductor and the influence such vacancies would have on the surface Fermi level; in Sec. III we present our numerical results; our conclusions are contained in Sec. IV.

II. ANION VACANCIES IN III–V SEMICONDUCTORS

In the bulk of a III–V semiconductor, an ideal anion vacancy (no lattice relaxation) induces twofold and sixfold degenerate levels (including spin) with symmetry a_1 and t_2, respectively.[7] The a_1 state occurs at lower energy than the t_2 state. There are three electrons associated with these bound (or resonant) levels in the neutral anion vacancy. Because the t_2 level is partially occupied (one electron) in the neutral vacancy, a Jahn–Teller distortion will occur. In Si, the vacancy with three electrons associated with the a_1 and t_2 states (positively charged in Si) is known to undergo a tetragonal Jahn–Teller distortion.[8] We assume that the distortion for the anion vacancy in the III–V semiconductors is also tetragonal. In this case, the symmetry of the electronic states is reduced from T_d to D_{2d} and the t_2 level splits into a twofold degenerate b_2 level and a fourfold degenerate e level. The distortion is such that the b_2 level is at lower energy.

We consider three charge states of the anion vacancy V^+, V^0 and V^- with two, three and four electrons associated with the bound (or resonant) states, respectively. We describe the energies of these states in analogy with the vacancy in Si.[8,9] The energy zero is taken to be the V^+ state with no tetragonal distortion[10] and with the electrons which will bind to form the other charge states at the Fermi energy. The energies of the three states of interest can then be written as

$$E_+ = \tfrac{1}{2}kQ^2, \qquad E_0 = \tfrac{1}{2}kQ^2 + \epsilon - VQ - \mu,$$
$$E_- = \tfrac{1}{2}kQ^2 + 2(\epsilon - \mu - VQ) + u \quad (1)$$

Here Q is the displacement of a single atom in the tetragonal distortion, k is the lattice restoring force constant for the displacement, ϵ is the one-electron energy (relative to the valence band maximum) of the t_2 state of the neutral vacancy with no lattice distortion, V is the Jahn–Teller coupling coefficient for the distortion,[10] u is the electrostatic repulsion for the negatively charged vacancy and μ is the electron chemical potential. Physically, Q is fixed for each state to minimize the energy for that state. The minimum values for the energy are:

$$E_+ = 0, \qquad E_0 = \epsilon - \mu - V^2/2k,$$
$$E_- = 2(\epsilon - \mu) - 2V^2/k + u \quad (2)$$

For fixed μ, the charge state of the vacancy is determined by the least of E_+, E_0, E_-. As pointed out in Ref. 9, there is no value of μ for which the V^0 state is stable if $u < V^2/k$. For this condition, V^+ is stable if $\mu < \epsilon - V^2/k + u/2$ and the V^- is stable otherwise. If $u > V^2/k$, the neutral state may be stable. Under this condition, the V^+ is stable if $\mu < \epsilon - V^2/2k$, V^0 if $\epsilon - V^2/2k < \mu < \epsilon + u - 3V^2/2k$, and V^- if $\mu > \epsilon + u - 3V^2/2k$.

In the bulk, the chemical potential is fixed by shallow dopants. However, in the defect model for Schottky barrier

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formation, it is assumed that there is a large concentration of defects in a thin layer near the semiconductor surface. In this case, the position of the Fermi level relative to the band edges at the surface will be determined by the defects. For the case of a free surface (without a macroscopic metal overlayer) the defects near the surface will charge so as to compensate the charge in the depletion region of the semiconductor. From electrostatics, the Fermi level measured relative to the valence band maximum at the surface, μ_s, in n-type material is given by

$$\mu_s = \mu - \frac{2\pi e^2}{\epsilon_0}\frac{(N_+ - N_-)^2}{n_d} \tag{3a}$$

where

$$(N_+ - N_-) = N_v\left[\frac{e^{-E_+/kT} - e^{-E_-/kT}}{e^{-E_+/kT} + e^{-E_0/kT} + e^{-E_-/kT}}\right]. \tag{3b}$$

Here n_d is the donor concentration, ϵ_0 is the semiconductor dielectric constant and N_+, N_- and N_v are the number per unit area of positively charged, negatively charged and all vacancies, respectively. The vacancy energies are given in Eq. (2) where the one electron energy ϵ is measured relative to the surface band edges. In p-type material, n_d in Eq. (3a) is replaced with $(-n_a)$.

For a Schottky barrier with a macroscopic metal overlayer, the defects charge and form a dipole with their image charge in the metal. The charge state of the defects need not be opposite to that in the space charge region because the metal overlayer can screen the space charge. Taking the vacancies to lie in a plane a distance l from the metal surface, μ_s in n-type material is given by

$$\mu_s = (I_s - \chi_m) + D_I + \frac{4\pi e^2 l}{\epsilon_d}[(N_+ - N_-) + n_d x_d] \tag{4}$$

Here I_s is the semiconductor ionization potential, χ_m is the metal work function, x_d is the depletion length, D_I is a chemically induced dipole layer which may occur at the interface[11] and ϵ_d is the dielectric constant of the disordered region at the interface. In p-type material n_d in Eq. (4) is replaced with $(-n_a)$.

At room temperature, kT is very small compared to the energy scale of interest. Thus, the function $(N_+ - N_-)$ will charge very rapidly as μ_s moves past the stability points for the vacancy charge states. As a result, for a sufficiently high surface density of vacancies, μ_s will be pinned at one of the stability points. In Table I, we list the stability points at which the pinning occurs and the minimum surface density of vacancies required to pin for the various possibilities.[12] From this table, we see that the vacancy charge state and hence the relevant stability point at the free surface depends on the semiconductor doping. However, in the Schottky barrier case, the vacancy charge state and relevant stability point depends on $(I_s - \chi_m + D_I)$. Consequently, it is possible that μ_s may differ for the free surface of an n- and p-type semiconductor,[3,4] but doping does not significantly influence μ_s in a macroscopic Schottky barrier.

In order that μ_s be approximately equal for metals in which $(I_s - \chi_m + D_I)$ has opposite signs, it is necessary to charge the defect region with opposite polarities. Simple donors and acceptors can charge with only one sign. Thus a single donor or acceptor defect cannot account for the independence of μ_s on χ_m observed in the III–V semiconductors, whereas a level which can charge with either sign (such as the anion vacancy) can account for this observation.

III. RESULTS FOR ANION VACANCY LEVELS

In order to determine μ_s, it is necessary to know the parameters ϵ, V, k and u. In this section we estimate these parameters for various III–V semiconductors. We consider materials of different ionicity[13] and attempt to correlate the results of our calculation with measured values for μ_s. We find that ϵ, for anion vacancies, increases with semiconductor ionicity in a manner similar to the experimentally observed behavior of μ_s.[3,4] The other parameters are less strongly dependent on ionicity and lead to modest shifts in the position of the stability points. For example, in the calculations of Ref. 9, the V^0 state in Si is found to be unstable and the shift in stability point $(-V^2/k + u)$ is 0.21 eV. We also determine the one electron energies for anion vacancies near the (110)

TABLE I. Surface Fermi level and surface vacancy concentration to complete pinning for various conditions.

	V^0 stable		V^0 unstable	
	Schottky barrier	Free surface	Schottky barrier	Free surface
V^-	$\mu_s = \epsilon - (3V^2/2k) + u$ $N_V \geq \dfrac{\mu_s - (I_s - \chi_m + D_I)}{4\pi e^2 l/\epsilon_d}$ $\mu_s \geq I_s - \chi_m + D_I$	$\mu_s = \epsilon - (3V^2/2k) + u$ $N_V \geq \left[\dfrac{n_d\epsilon_0(\mu - \mu_s)}{2\pi e^2}\right]^{1/2}$ n-type	$\mu_s = \epsilon - (V^2/k) + (u/2)$ $N_V \geq \dfrac{\mu_s - I_s + \chi_m - D_I}{4\pi e^2 l/\epsilon_d}$ $\mu_s > I_s - \chi_m + D_I$	$\mu_s = \epsilon - (V^2/k) + (u/2)$ $N_V \geq \left[\dfrac{n_d\epsilon_0(\mu - \mu_s)}{2\pi e^2}\right]^{1/2}$ n-type
V^0	$\mu_s = I_s - \chi_m + D_I$ $N_V \geq 0$ $\epsilon - \dfrac{V^2}{2k} \leq \mu_s \leq \epsilon - \dfrac{3V^2}{2k} + u$	$\mu_s = \mu$ $N_V \geq 0$ $\epsilon - \dfrac{V^2}{2k} \leq \mu_s \leq \epsilon - \dfrac{3V^2}{2k} + u$		
V^+	$\mu_s = \epsilon - (V^2/2k)$ $N_V \geq \dfrac{I_s - \chi_m + D_I - \mu_s}{4\pi e^2 l/\epsilon_d}$ $\mu_s \leq I_s - \chi_m + D_I$	$\mu_s = \epsilon - (V^2/2k)$ $N_V \geq \left[\dfrac{n_a\epsilon_0(\mu_s - \mu)}{2\pi e^2}\right]^{1/2}$ p-type	$\mu_s = \epsilon - (V^2/k) + (u/2)$ $N_V \geq \dfrac{I_s - \chi_m + D_I - \mu_s}{4\pi e^2/\epsilon_d}$ $\mu_s < I_s - \chi_m + D_I$	$\mu_s = \epsilon - (V^2/k) + (u/2)$ $N_V \geq \left[\dfrac{n_d\epsilon_0(\mu_s - \mu)}{2\pi e^2}\right]^{1/2}$ p-type

semiconductor surface. In this case, the highest occupied level in the neutral vacancy is the state of interest. It is partially filled (one electron in a twofold degenerate state) and is the state which will be involved in charging the vacancy.

Our calculations are performed in the tight binding approximation. We consider GaAs, InP, and $Ga_{1-x}Al_xAs$. Calculational details are included in Ref. 14. Our results for GaAs and InP are shown in Fig. 1. On the fifth layer from the surface, the energy levels are essentially the same as those in the bulk of the semiconductor. There are two bound (or resonant) levels; the a_1 level is occupied with two electrons and the higher t_2 level has one electron in the neutral vacancy. As the vacancy is moved toward the surface, there is no significant change[15] in the energy levels until the vacancy reaches the second atomic layer from the surface. There the t_2 level splits into three nondegenerate levels and they move to lower energy. The arrow indicates the highest occupied level in the neutral vacancy. For the vacancy on the surface layer, one of the bound state levels is lost. The loss occurs because only three bonds are broken in the surface vacancy and hence only three bound states can be made. The energy levels are first significantly perturbed at the second atomic layer because there a vacancy has a nearest neighbor on the surface layer. Because of reconstruction, the hybridization of the surface cation orbitals involved in the bonding is sp^2 rather than sp^3 as in the bulk. As a result, in forming the anion vacancy on the second atomic layer from the surface, a sp^2 bond is broken. The dangling sp^2 orbital is of lower energy than the dangling sp^3 orbitals making up the bulk vacancy states because the sp^2 orbital has a larger s state component. On the surface layer,

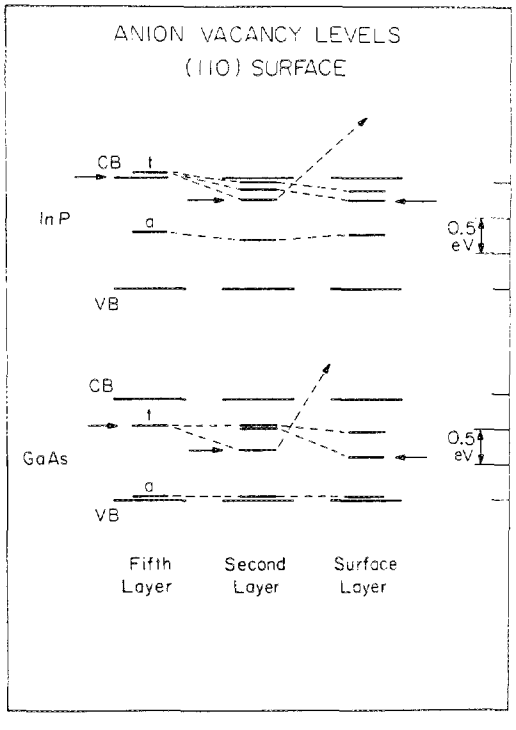

FIG. 1. Energy positions, relative to the band edges, of ideal anion vacancies near the (110) surface of InP and GaAs. The bound state energy levels are essentially the same as those in the bulk until the vacancy reaches the second atomic layer from the surface. The arrows indicate the highest energy state occupied in the neutral vacancy.

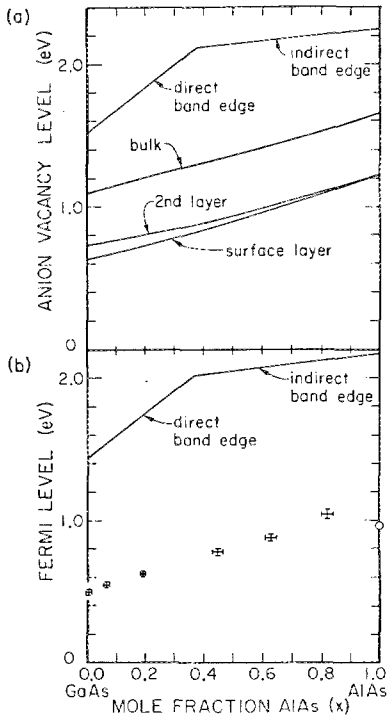

FIG. 2. (a) Position of the highest occupied state in the neutral anion vacancy as a function of alloy composition in $Ga_{1-x}Al_xAs$. Results for vacancies in the bulk, second atomic layer, and on the (110) surface are shown. The energy zero is the valence band maximum; the calculated position of the conduction band minimum is also shown.

(b) Measure position of the surface Fermi level as a function of alloy composition in $Ga_{1-x}Al_xAs$. The measurements are from Ref. 16.

two sp^2 bonds are broken and again the bound states are at lower energy than the bulk.

Comparing the results for InP with those of GaAs, we see that the anion vacancy levels in InP are at higher energy relative to the band edges. This upward shift in the energy levels occurs because InP is more ionic than GaAs. In covalent materials, the gap between valence and conduction band states is primarily due to the splitting of bonding and antibonding states. In the more ionic materials, the valence band states are primarily anion-derived and the conduction band states are more strongly cation-derived. For the covalent case, the cation dangling bonds from the anion vacancy will appear between the bonding and antibonding states, that is, near midgap. For more ionic materials, the cation dangling bond states will move toward the cation-derived states of the conduction band. Thus the vacancy levels in GaAs occur at lower energy than the corresponding states in the more ionic InP. It is interesting to note that measured values of μ_s in III–V semiconductors show a trend similar to that calculated for the anion vacancy levels. In the series GaSb, GaAs, and InP (listed in order of increasing ionicity), μ_s is observed to increase from near the valence band maximum to near the conduction band minimum.[3,4]

In Fig. 2, we show the calculated position of the highest occupied level in the neutral anion vacancy in the bulk, second atomic layer and on the (110) surface of $Ga_{1-x}Al_xAs$ as a function of alloy composition. The position of these levels, relative to the valence band maximum is an increasing function of the concentration of the more ionic AlAs. The energy of the highest occupied level in the neutral anion vacancy on the surface and second layers are quite close to each other, whereas this level on the third layer (not shown explicitly) is close to that of the bulk. This occurs because the vacancy states on the surface and second layers are made heavily from dangling bond orbitals of a surface Ga which is

SP^2-hybridized whereas those in the third and deeper layers are made heavily from dangling bond orbitals on Ga atoms off the surface which are SP^3 hybrids. In Fig. 2 we also show the measurements of Ref. 16 for μ_s in $Ga_{1-x}Al_xAs$ as a function of x. We note that there is a strong similarity between the calculated positions of the highest filled neutral anion level and the measured position of μ_s.

We estimate the Jahn–Teller coupling coefficients V and the Coulomb repulsion u in the bulk using perturbation theory. The unperturbed wave-function can be written as

$$\psi_\beta(r) = \sum_{\alpha j} C^\beta_{\alpha j}(\epsilon_\beta)\, A_{\alpha j}(r), \tag{5a}$$

where

$$C^\beta_{\alpha j}(\epsilon_\beta) = \frac{G_{\alpha j;\beta 0}(\epsilon_\beta)}{[-G'_{\beta 0;\beta 0}(\epsilon_\beta)]^{1/2}}. \tag{5b}$$

Here α labels an atomic function and j gives the atomic position, G is the Green's function, ϵ_β is the energy of the unperturbed state (a t_2 state is of interest here, in this case β indicates a P orbital), the prime in Eq. (5b) indicates an energy derivative and A is an atomic function. The Jahn–Teller coupling coefficient is calculated from

$$VQ = \langle \psi_\beta \left| \frac{\partial H}{\partial Q} Q \right| \psi_\beta \rangle, \tag{6}$$

where Q is the tetragonal normal mode displacement. The distortion potential, $\partial H/\partial Q$ is found by assuming that the tight binding parameters scale like the overlap of the atomic functions. For GaAs and AlAs, the tetragonal distortion coupling coefficients for the b_2 state are 1.3 eV/Å and 0.7 eV/Å, respectively. The e states shift in the opposite direction by half those amounts. The Coulombic repulsion was estimated as

$$u = \langle \psi_\beta(r_1)\psi_\beta(r_2) \left| \frac{e^2}{\epsilon(r_{12})|r_{12}|} \right| \psi_\beta(r_1)\psi_\beta(r_2) \rangle, \tag{7}$$

where $[e^2/\epsilon(r)\, r]$ is the Fourier transform of $(4\pi e^2/\epsilon(q)\, q^2)$ and $\epsilon(q)$ is the dielectric function. One center integrals on the first and second atomic shells were included in the estimate of u. The results were 0.20 eV and 0.27 eV for GaAs and AlAs, respectively. The force constant k, was estimated by scaling the Keating model calculations of Ref. 9 for Si by the bond stretching force constant determined from compressibility.[17] The result of this scaling was 12 eV/Å^2 for both GaAs and AlAs (compared with 14.8 eV/Å^2 for Si[9]).

These values for the parameters indicate that there is a small stability region for the neutral anion vacancy in GaAs and AlAs. However the accuracy of the estimates is not great enough to settle this issue. From our point of view, the important thing is that the qualitative behavior of the one electron energies shown in Fig. 2 is not greatly modified. For the V^+ stability point the GaAs end point is shifted down by 0.07 eV and the AlAs end point down by 0.02 eV as compared with Fig. 2 while for the V^- stability point the GaAs end point is unchanged and the AlAs endpoint is shifted up by 0.2 eV. Thus in both cases the slope of the bulk line in Fig. 2 is slightly increased. We are currently investigating the effects of lattice relaxation for vacancies on the surface. We expect results analogous to those in the bulk.

Hence, with Jahn–Teller distortions and Coulomb corrections included, we still see a strong similarity between the calculated position of the anion vacancy levels and the measured values for μ_s. There is, of course, some uncertainty in the absolute energy levels but we think that the trends are significant.

IV. CONCLUSIONS

We presented a calculation of energy levels of anion vacancies close to the (110) surface of III–V semiconductors. We have found that energy levels are not significantly changed until the vacancy reaches the second atomic layer from the surface. As one considers more ionic III–V semiconductors, the anion vacancy levels move to higher energy relative to the valence band maximum. There is a correlation between the calculated anion vacancy levels and the measured values of μ_s in III–V semiconductors. This correlation will probably be maintained if one considers other defect levels formed from cation dangling bonds. This correlation suggests that the defect model is a promising model of Schottky barrier formation.

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